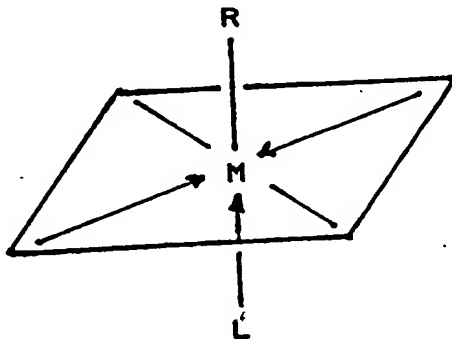


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08F 4/80 // C08F 2/38	A1	(11) International Publication Number: WO 87/ 03605 (43) International Publication Date: 18 June 1987 (18.06.87)
(21) International Application Number: PCT/AU86/00372 (22) International Filing Date: 3 December 1986 (03.12.86) (31) Priority Application Number: PH 3694 (32) Priority Date: 3 December 1985 (03.12.85) (33) Priority Country: AU (71) Applicant (for all designated States except US): COMMON-WEALTH SCIENTIFIC & INDUSTRIAL RESEARCH ORGANIZATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only): HAWTHORNE, David, Geoffrey [AU/AU]; 46 Gowrie Street, South Oakleigh, VIC 3167 (AU). (74) Agents: CORBETT, Terence, Guy et al.; Davies & Collison, 1 Little Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>

(54) Title: OLIGOMERIZATION PROCESS**(57) Abstract**

Oligomers are produced from unsaturated monomers. They contain terminal unsaturation and have a degree of polymerization of from 2 to 200. These oligomers are produced by the free radical polymerization of unsaturated monomers using as an initiator and/or chain transfer agent in the process a transition metal complex comprising a metal cation and at least one chelating agent, said transition metal complex being generally in accordance with formula (I), wherein M is a transition metal ion which can form hexa- or penta-coordinated structures and, when complexed in this manner, has two or more readily interconverted adjacent valence states, R is hydrogen or an organic group or a transition metal complex derived from formula (I) and L is a ligand for controlling the stability and electron transfer properties of the transition metal complex and consists of an electron pair donor (Lewis base) capable of coordination with the metal ion.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

"OLIGOMERIZATION PROCESS"

This invention relates to processes for radical-mediated polymerization of unsaturated species, and for the control or limitation of the molecular weights of the polymeric products produced from such processes. Polymers of limited molecular weights, or
5 oligomers, are useful as precursors in the manufacture of other polymeric materials, and as additives in plastics, elastomerics, and surface-coating compositions, as well as being useful in their own right
10 in many applications..

In conventional polymerization practice, manufacture of oligomers requires the use of a free radical source, the initiator, and of a chain-transfer agent. The chain-transfer agent controls the molecular
15 weight of the polymer molecules by reacting with the propagating radical species to terminate its growth and later initiates a new polymer chain thus transferring the growth process from one discrete polymer molecule to another discrete polymer molecule. At least a part of
20 the chain-transfer agent is incorporated into the polymer molecules, and thus is consumed during the process which may result in undesirable increases in average molecular size and polydispersity of the

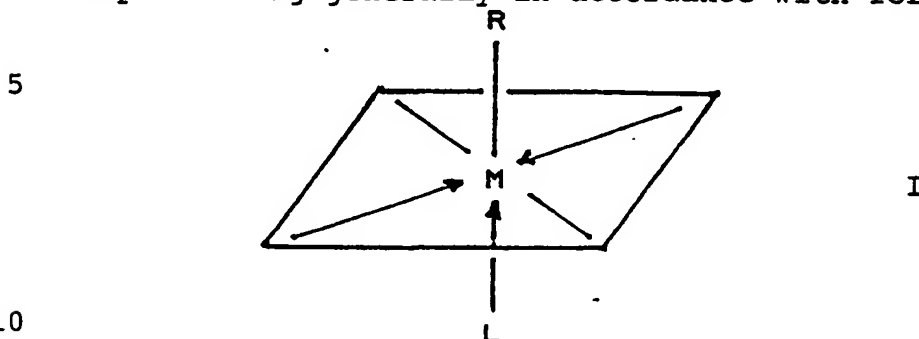
product. The incorporated residue of the chain transfer agent can also lead to undesirable end-groups on the polymer.

Transition metal complexes are widely used as
5 polymerization agents, but principally as catalysts or coagents in redox radical initiation systems, for example, with organic peroxides for the curing of styrene/unsaturated polyester formulations, or in the initiation of ionic polymerization, for example, of
10 epoxides. Transition metal complexes have also been used for the control of stereochemistry and the inhibition of crosslinking (gel formation) in the polymerization of butadiene and other olefins. Transition metal complexes, including species related to
15 those described in the specification have also been used as catalysts for the hydrogenation or oxidation of organic compounds.

We have now discovered that certain transition
metal complexes can act as thermal or photochemical
20 radical initiators and also as chain-transfer catalysts for the control of molecular weight in radical-mediated homogeneous polymerizations. Unlike the conventional chain-transfer agents, the agents described in this specification are not consumed during the polymerization
25 process, thereby resulting in more efficient useage with no residues as end-groups, and improved control of the molecular weights of the products.

According to one aspect of the present invention there is provided a process for the free radical
30 polymerization of unsaturated monomers which comprises using as an initiator and/or chain transfer agent a

transition metal complex comprising a metal cation and at least one chelating agent, said transition metal complex being generally in accordance with formula I



wherein M is a transition metal, R is hydrogen or an organic group or a transition metal complex derived from formula I, and L is a ligand for controlling the stability and electron transfer properties of the transition metal complex, and consists of an electron pair donor (Lewis base) capable of coordination with the metal ion.

Typical transition metal complexes are illustrated in the accompanying drawings, and described below.

20 In one form, the transition metal complexes which are useful in the process of the present invention comprise a metallic cation (M) coordinated with a planar (equatorial), or approximately planar, arrangement of chelating ligands, with one or two axial ligands as shown by formula I. One of the axial ligands (R in formula I) consists of a hydrogen atom or an organic moiety bound by a labile carbon-metal bond to the transition metal. The other ligand (L in Formula I) is an electron pair donor, as defined above.

Alternatively, the transition metal complex may have the related dimeric structure of formula II, in which the group R of formula I comprises a second chelated metal ion, and which is capable of dissociation to form (or may exist in equilibrium with) the monomeric species III and is capable of reaction with radicals or other species present in the polymerizing system to form intermediates functionally equivalent to those of formula I. The second chelated metal ion may be the same or different from the first metal ion.

The transition metal ion may be any of those which can form hexa- or penta-coordinated structures as described and which, when complexed in this manner, have two or more readily interconverted adjacent valence states. Cobalt ions are particularly useful, but those of other metals such as rhenium or iridium may be employed.

The equatorial coordination may be obtained from a single quadridentate chelating ligand, from two bidentate ligands, or from one bidentate ligand plus two monodentate ligands, or any other appropriate combination of ligands. The chelation may involve both ionic/covalent bonding and coordinative bonding between the ligand and the metal ion and should preferably result in a complex which has no nett ionic charge and is soluble in non-polar or polar organic solvents. The complexes may include ligands which can give rise to ionized complexes through protonation or deprotonation of the ligand, for example, of the bridging hydroxo groups of the bis(dimethyl glyoxime) cobalt chelate (formula IV in the drawing) or which bear other

ionizable groups. Suitable chelating ligands may consist of dioximes or other dicarbonyl or enolic carbonyl derivatives, or hydroxy, carboxy or enolic derivatives of azomethines (Schiff bases), such as

5 salicylaldehyde-diamine (formula V) or acetylacetone-diamine (formula VI) condensates. Complexes formed from dioximes, such as dimethylglyoxime (formula IV, R' = methyl), or derivatives in which the bridging hydrogens (formula IV) are replaced by

10 difluoroborato groups, are also useful.

The covalently-bound axial organic group (R) may consist of an alkyl, aryl, or heterocyclic species, or of substituted derivatives of these species which are capable of homolytic dissociation from the metal ion on

15 heating or on irradiation with visible or ultraviolet light. Alkyl derivatives bearing one or more substituents on the carbon bonded to the metal ion are particularly useful; such substituents may include nitrile, ester, aromatic and substituted aromatic

20 groups. However, any suitable substituent group may be employed. Alternatively, the group (R) may consist of a halide or other anion bound to the chelated metal.

The axial ligand (L) can be, for example, water, an alcohol or other hydroxylic species, a thioether, amine,

25 phosphine, carbonyl or carboxylate, or any other species which does not inhibit dissociation of the opposing axial ligand. Particularly useful ligands include weakly basic tertiary amines such as pyridine or substituted pyridines. The ligand L may also be derived

30 in situ from the monomer or another species present in the polymerization mixture. Therefore, useful agents

may also include species which lack the axial ligand (L), such as the Schiff's base chelates described in Examples 14 to 16, when used in formulations containing a suitable base as an ingredient.

5 Methods for the preparation of planar chelation complexes of transition metals, such as those useful in the present invention, are widely known, and methods for the preparation of suitable derivatives thereof, such as those bearing labile covalently bound axial ligands have
10 also been described in the chemical literature. Any conventional or suitable method of making the transition metal complexes for use in the present invention may be used. Some suitable methods are described in Examples 1, 8 and 9 hereinafter.

15 In another aspect, the present invention provides a process for the free-radical polymerization of unsaturated monomers using the above described transition metal complexes as initiators and chain
transfer agents. Suitable unsaturated monomers include
20 methacrylate esters, vinyl esters, vinylaromatics, or mixtures of these; they may also include acrylic esters, other vinyl derivatives and unsaturated species susceptible to free-radical induced polymerization. The polymerization of methacrylate esters and styrene appear
25 to be the most susceptible to catalytic chain transfer using the agents of this invention, whilst less susceptible monomers, for example, acrylate esters, may require the addition of methacrylates as comonomers for transfer to be effective.

30 Some oxime derivatives (e.g. formula IV) or the active chain transfer intermediates derived therefrom

may be susceptible to hydrolysis and resultant loss of catalytic activity. The difluoroborato derivatives (Example 10) are more resistant to hydrolysis, and can be used for the preparation of acidic oligomers, such as methacrylic acid polymers and copolymers.

The use of the chain transfer catalysts, in accordance with the present invention, for the control of molecular weight typically involves the following procedure. The transition metal complex is dissolved in a mixture of monomer or monomers and inert solvent, and heated or exposed to actinic light under an inert atmosphere to initiate the polymerization reaction. The molecular weight of the product can be altered by altering the ratio of complex to monomer in the polymerization formulation, or the reaction temperature. The complexes described in this specification, and their byproducts, can be removed by filtering the product solution through a layer of silica, to which they are generally strongly adsorbed. The efficiency of the polymerization process can be enhanced by addition of non-oxidizing initiators, such as azo-derivatives, to the polymerization formulation to compensate for propagating radicals which are destroyed by bimolecular recombination or disproportionation, reactions which proceed in competition with the propagation and chain-transfer reactions.

The oligomers produced in accordance with the present invention generally have a degree of polymerization of from 2 to 200. They are unique in that they contain reactive terminal unsaturation which can undergo known reactions for unsaturated groups. For

example, they may be reduced by catalytic hydrogenation, or be utilized in subsequent copolymerization with other unsaturated monomers, especially vinylic or acrylic monomers, or be modified by chemical reaction to produce
5 other functional oligomers.

The present invention will now be described more fully with reference to the following examples.

Unless otherwise stated, molecular weights of products described in the Examples are number-average
10 polystyrene-equivalent molecular weights. The acronyms MMA and AIBN refer respectively to methyl methacrylate and azobisisobutyronitrile.

Example 1

Bis-[(2,3-butanedione dioximato) (1-)N,N'] (1-
15 cyano-1-methylethyl) (pyridine)cobalt(III), Agent 1, was prepared using a well known general procedure: cobaltous acetate tetrahydrate (25 g) and dimethylglyoxime (23.2 g) were dissolved in deaerated methanol (325 ml) under a nitrogen atmosphere, and the mixture stirred at 20°C for
20 1 hour. Deaerated methacrylonitrile (8.5 g) was then added and the nitrogen atmosphere replaced with hydrogen at atmospheric pressure. The mixture was then vigorously stirred whilst deaerated pyridine (8 g) was added. Stirring was continued until 1.0 to 1.2 l of
25 hydrogen had been adsorbed, after which the mixture was filtered and diluted with cold water (ca. 800 ml). The Agent 1 crystallized as deep orange platelets, yield 26 g.

A deoxygenated mixture of MMA (2 ml), benzene (8
30 ml) and Agent 1 (95 mg) was heated at 60°C for 30 hours. After cooling, the acicular crystals of chelate dimer

which formed during the reaction were separated, and the remaining chelate byproducts removed by adsorption in silica to produce a colorless solution containing 1.2 g of oligo-MMA, consisting largely of the dimer, plus a
5 small proportion of trimer. Similar treatment of methyl methacrylate in the absence of Agent 1 yielded negligible amounts of polymer. The byproduct chelates are rapidly oxidised on exposure to air, forming dark-colored species which could also be readily removed
10 from the solution by adsorption on silica.

Example 2

Bis-[(2,3-butanedione dioximato)(1-*N,N'*)(1-cyano-ethyl)(pyridine)cobalt(III)], Agent 2, was prepared using the method of Example 1, with acrylonitrile (7.4 g)
15 instead of the methacrylonitrile.

A deoxygenated mixture of MMA (5 ml) and Agent 2 (20 mg) in benzene (10 ml) was exposed to near-UV light from an 80W filtered high-pressure mercury lamp for 3 hours. The chelate byproducts were then removed by
20 adsorption on silica, and the product solution distilled under vacuum, yielding 0.5 g of MMA dimer.

Example 3

A deoxygenated mixture of MMA (4 ml) and Agent 1 (1.2 mg) in benzene (6 ml), with AIBN (20 mg) as
25 coinitiator, after heating at 60°C for 36 hours, yielded 1.7 g of oligo-MMA having a molecular weight of 250. A similar treatment of MMA in the absence of Agent 1 yielded a polymer having a molecular weight of 87000, whilst use of 0.5 mg or 0.1 mg of the Agent yielded
30 oligomers having molecular weights of 450 or 5100 respectively and a polydispersity ratio (MW/MN) of ca.

1.6. A similar treatment using 0.5 mg of Agent 1, but at 70°C, yielded oligomers having a molecular weight of 300.

Example 4

5 A series of deoxygenated mixtures of monomer (2 ml) and AIBN (30 mg) in benzene (8 ml), with or without Agent 1 (5 mg), after heating at 60°C for 36 hours, yielded polymers having the molecular weights shown in the Table.

10

Monomer	With Agent 1	Without Agent 1
Methyl methacrylate	250	18,000
n-Butyl methacrylate	300	25,000
15 Methacrylonitrile	Dimer	High polymer
Styrene	500	10,000
Vinyl acetate	15,000	216,000
Ethyl acrylate	82,000	111,000

20 A similar polymerization of styrene, but using either Agent 1 or Agent 2, with toluene as solvent and 1,1-azobis(1-cyanocyclohexane) as initiator at 95°C, yielded a mixture of styrene dimer and trimer; polymerization in the absence of the Agent yielded
 25 polymer with a molecular weight of 13,700.

Example 5

Analogues of Agent 1, but with ligands (L) of different basicity were prepared using the method of Example 1, replacing the pyridine with the more-basic
 30 4-t-butylpyridine (5 ml), to form Agent 3, or with less-basic 4-cyanopyridine (6 ml) to form Agent 4. These

Agents were used in polymerization of styrene according to the method of Example 4, the reaction in the presence of Agent 3 yielding an oligomeric mixture with molecular weight of 500, whilst a similar treatment using Agent 4 produced an oligomer having molecular weight of 2000. Polymerization of MMA in the presence of either reagent yielded predominantly MMA dimer.

Example 6

A series of mixtures containing MMA and a comonomer were treated with by the method of Example 4. The comonomer proportions and the molecular weights of the copolymers are shown in the Table:

	Comonomer	MMA	Mol. Wt.
15	Ethyl acrylate, 0.5 ml	1.5 ml	6,800
	Ethyl acrylate, 1.0 ml	1.0 ml	30,000
	Ethyl acrylate, 1.5 ml	0.5 ml	66,000
	Methacrylonitrile, 1.0 ml	1.0 ml	dimers
20	Glycidyl methacrylate, 1.0 ml	1.0 ml	dimers

A similar treatment of a mixture of hydroxyethyl methacrylate (0.5 ml) and MMA (2 ml) in benzene (5 ml), with Agent 1, (1 mg) yielded a polymer having molecular weight of 5,500. Treatment in the absence of the Agent yielded a polymeric gel.

Example 7

Bis-[(2,3-butanedione dioximato)(1-)N,N'] (1-ethoxycarbonyl)ethyl)-(pyridine)cobalt(III), Agent 5, was prepared using the method of Example 1, using ethyl acrylate (5 g) instead of the methacrylonitrile.

Treatment of MMA with the Agent yielded an oligomeric mixture consisting predominantly of the dimer.

Example 8

Bis-[(2,3-butanedione dioximato) (1-)N,N'] (2-ethoxy-
5 carbonylethyl-(pyridine)cobalt(III), Agent 6, was prepared by the following method. A mixture of cobaltous chloride hexahydrate (11.9 g), and dimethylglyoxime (11.6 g) was dissolved, with stirring, in deaerated 90% ethanol (200 ml) under nitrogen. The
10 following deaerated reagents were then added in sequence: sodium hydroxide (4 g in 25 ml water), pyridine (4 g), ethyl acrylate (5 g), sodium hydroxide (1 g in 16 ml water). The resultant mixture was stirred for 5 minutes and then poured into water (500 ml)
15 containing acetic acid (2.5 ml). The Agent was recovered by extraction of the aqueous mixture with methylene chloride, evaporation of the extract, and recrystallization of the residue from aqueous methanol.

Treatment of MMA (1.9 g) with Agent 6 at 60°C by
20 the method of Example 4 yielded a mixture of oligomers consisting of dimer (0.8 g), trimer (0.6 g), plus higher oligomers.

Example 9

Bis-[(2,3-butanedione dioximato) (1-)N,N'] (2-methyl-
25 ethyl) (pyridine)cobalt(III), Agent 7, was prepared by the following method. A mixture of cobaltous chloride hexahydrate (17.2 g), dimethylglyoxime (17.2 g) was dissolved, with stirring, in deaerated methanol (200 ml) under nitrogen. Sodium hydroxide (6 g in 6 ml water)
30 and pyridine (6 g) was then added, the resultant mixture cooled to, and maintained at -10°C. The chilled mixture

was stirred for 15 minutes and then sodium hydroxide (3 g in 3 ml water) was added, followed by the slow addition of sodium borohydride (0.4 g in 5 ml water). After stirring a further 15 minutes, isopropyl bromide
5 (6.8 g) was added, and the mixture allowed to warm to room temperature. The bulk of the solvent methanol was removed by vacuum evaporation, and the residue added to chilled water (200 ml) containing pyridine (2 ml); the Agent crystallized on standing of the chilled solution
10 and was recrystallized from aqueous methanol.

The methyl analogue of Agent 7, Agent 8, was prepared using a similar procedure, except that the isopropyl bromide was replaced by methyl sulphate (10.1 g).

15 MMA was treated at 70°C with the Agents using the method of Example 4. Treatment with Agent 7 yielded MMA dimer, whilst treatment with the less active Agent 8 yielded a mixture of dimer, trimer, and higher oligomers.

20 Example 10

[Bis[μ -[(2,3-butanedione dioximato)(2-)O:O']-tetra-fluorodiborato(2-)-N,N',N'',N'''] (2-methylethyl) (pyridine)cobalt(III), Agent 9, was prepared as follows. Agent 7 (10 g) was dissolved in a mixture of boron
25 trifluoride etherate (15 ml) and dry ether (90 ml), and then cooled in an ice-bath whilst pyridine (8.6 ml) was slowly added. The resultant suspension was stood at 20°C for 2 days, after which the solids were removed, the ethereal solution evaporated, and the residue, Agent
30 9, recrystallized from acetone.

A mixture of MMA (2 ml), Agent 9 (5 mg), AIBN (25 mg), and ethanol (8 ml) was heated at 60°C for 36 hours. The cobalt chelate was then removed by adsorption on silica, and the ethanolic solution evaporated to yield the products, MMA dimer. A similar treatment of MMA using Agent 7 yielded a mixture of dimer and trimer, whilst treatment without addition of the Agent resulted in the formation of ethanol-insoluble poly(MMA) of high molecular weight. A similar treatment of MMA with Agent 9 using a mixture of ethanol (7.5 ml) and acetic acid (0.5 ml) as solvent also resulted in the formation of predominantly dimeric MMA, whereas treatment with Agent 7 (or Agent 1) in the acidic solvent mixture yielded products containing poly(MMA).

A deoxygenated mixture of MMA (1 ml) and methacrylic acid (1 ml) with AIBN (20 mg) and Agent 9 (1 mg) in ethanol (8 ml) was heated at 80°C for 24 hours. The cobalt chelate was removed by adsorption on silica and the solution evaporated to yield a viscous oligomeric product having a molecular weight (after exhaustive methylation with diazomethane) of 470. A similar treatment of methacrylic acid yielded a solid oligomer with a (methylated) molecular weight of 550.

Example 11

Bis-[(2,3-butanedione dioximato)(1-)N,N'] (pyridine)cobalt(II), Agent 10, was prepared by dissolving a mixture of cobaltous acetate tetrahydrate (5 g) and dimethylglyoxime (4.6 g) in deaerated methanol (80 ml) containing pyridine (1.6 g) under oxygen-free nitrogen. After stirring for 1 hour, the crystalline Agent was removed by filtration, washed on the filter with

methanol, and then dried in vacuum. All operations were conducted with rigorous exclusion of air, and the product stored under nitrogen as the solid Agent 10 and its solutions are rapidly oxidised on exposure to
5 atmospheric oxygen.

- The triphenylphosphine analogue of Agent 10, Agent 11, was prepared by a similar method, using triphenylphosphine (5.3 g) instead of the pyridine.

Solid agent 11 is less susceptible to oxidation
10 that Agent 10, although its solutions are still rapidly oxidised on exposure to air. Treatment of MMA with either agent using the method of Example 4 resulted in the formation of MMA dimer.

Example 12

15 Bis-[(2,3-butanedione dioximato) (1-)N,N'] (chloro)-(pyridine)cobalt(III), Agent 12, was prepared as follows. A mixture of cobaltous chloride hexahydrate (5 g) and dimethylglyoxime (5.5 g) was dissolved in hot ethanol. Pyridine (3.5 g) was then added, the mixture
20 cooled to 20°C, and aerated for 1 hour. The crystallized Agent was then removed by filtration, washed successively with water and alcohol, then dried in vacuum at 20°C.

Treatment of MMA with the Agent at 60°C using the
25 method in Example 10 produced a mixture of oligomers containing MMA dimer and higher oligomers. The cobalt chelate byproducts were not readily adsorbed on silica. A similar treatment at 80°C yielded a mixture of MMA dimer and trimer.

30 Treatment of a mixture of ethyl acrylate (1 ml), methyl methacrylate (1 ml) with the Agent at 80°C using

the method in Example 10 yielded a copolymer having molecular weight of 4,200 and polydispersity of 2.2. A similar treatment in the absence of the Agent yielded copolymer having a molecular weight of 24,300.

5 Example 13

Bis-[(1,2-diphenylethanedione dioximato) (1-)-N,N']-(2-methylethyl) (pyridine) cobalt(III), Agent 13, was prepared as follows. A mixture of dehydrated cobaltous chloride (1.3 g), benzil dioxime (4.8 g) and pyridine
10 (0.79 g) was heated with aeration on a steam bath until the mixture no longer had a blue-green coloration. The precipitated chlorocobalt(III) chelate was removed, washed with methanol, and then dried in air. The dried solid (6.2 g) was suspended in methanol (80 ml), and the
15 suspended purged with, and maintained under nitrogen. A solution of potassium hydroxide (1.2 g in 20 ml methanol) was added and the mixture cooled with stirring to -10°C. A solution of sodium borohydride (0.14 g in 2 ml water) was added, followed by, after stirring for 15
20 minutes, isopropyl bromide (1.2 ml). The mixture was then allowed to warm to 20°C and the sparingly soluble Agent 13 removed by filtration, washed with water, then with water containing 10% pyridine, and dried in-vacuo over calcium chloride.

25 MMA was treated with the Agent using the method of Example 4, to yield dimeric MMA. In this example, adsorption of the cobalt chelate byproducts on silica was incomplete.

In the following Examples:

30 Acacen is [[4,4'-(1,2-ethanediyldinitrilo)-bis-pentanato] (2-)-N,N',O,O']

Salen is [[2,2'-[1,2-ethanediylbis(nitrilomethylidene)bis[phenolato]](2-)-N,N',O,O']

Example 14

(Salen)cobalt(II), Agent 14, was prepared as follows. Cobaltous acetate tetrahydrate (13.9 g) and (14.9 g) of salen (prepared by the condensation reaction between salicylaldehyde (2 mol) and ethylene diamine (1 mol)) was dissolved in nitrogen-purged methanol (185 ml). The mixture was warmed to complete the dissolution, and the Agent crystallized on cooling of the solution. The air-sensitive Agent was washed with deaerated water and then dried in-vacuo at 80°C; it was stored in-vacuo and handled under a nitrogen atmosphere.

MMA was treated with a mixture of Agent 14 (5 mg) and pyridine (8 mg) using the method of Example 4, yielding a polymer having molecular weight of 3,400 and polydispersity 1.8. A similar treatment without addition of pyridine yielded a polymer having molecular weight of 8,300, whilst treatment in the absence of the Agent or pyridine yielded polymer of molecular weight 18,000.

Example 15

Ethyl(salen)cobalt(III), Agent 15, was prepared as follows, all reactions being conducted with deaerated reagents under a nitrogen atmosphere. A mixture of salicylaldehyde (7.2 g) and ethylene diamine (3.0 g) was dissolved in methanol (400 ml), cobaltous chloride hexahydrate (11.9 g) added, and the mixture stirred until the salt dissolved. Sodium hydroxide (4 g in 4 ml water) was added and the mixture cooled to -10°C. After 10 minutes, additional sodium hydroxide (7.5 g in 7.5 ml

of water) was added, followed by sodium borohydride (1 g in 10 ml methanol) and palladous chloride (1 ml of 2% solution in 1M KCl). After 10 minutes, ethyl bromide (10 ml) was added and, 5 minutes later, any residual borohydride destroyed by the addition of acetone (15 ml). The mixture was allowed to warm to room temperature, then filtered, and the filtrate diluted with water (750 ml) containing pyridine (10 ml). The Agent crystallized as orange platelets on standing of the chilled aqueous solution. Unlike the oxime-based agents, Agent 15 crystallizes as a labile hydrate or as an anhydrous dimeric species. The Agent dissolves in non-basic organic solvents to form a green solution which is converted to the orange base-ligated species on addition of bases such as pyridine.

Treatment of MMA with Agent 15 (5 mg) by the method of Example 4, with the addition of pyridine (10 mg), yielded poly(MMA) with molecular weight of 4,100. Treatment in the absence of pyridine yielded a polymer, molecular weight 12,900, whilst treatment in the absence of Agent or pyridine produced polymer having molecular weight of 18,000.

Example 16

Aquo(ethyl)(acacen)cobalt(III), Agent 16, was prepared by the following method. Cobaltous chloride hexahydrate (4.8 g) was dissolved in 20 ml of deaerated water under nitrogen. 4.5 g of (acacen), prepared by condensation of acetylacetone (2 mol) and ethylene diamine (1 mol), was then added, followed by sodium hydroxide (1.6 g). The mixture was heated, with stirring, until the suspended solid turned to a

yellow-orange colour. The mixture was then cooled, the intermediate, (acacen)cobalt(II) filtered off under nitrogen and washed on the filter with warm deaerated water (10 ml), and then dried in-vacuo over calcium chloride. The air-sensitive anhydrous chelate (4.5 g) was dissolved in anhydrous tetrahydrofuran maintained under argon. Sodium amalgam (0.38 g sodium in 5 g mercury) was added, and the mixture stirred vigorously for 2 hours, then cooled to -10°C . Ethyl bromide (1.4 m) was added and the mixture stirred for 15 minutes, then decanted from the amalgam residues into water (100 ml). Agent 16 separated as brown crystals when the tetrahydrofuran was stripped under vacuum at 20°C ; it was purified by dissolution in acetone and crystallization on addition of water to the resultant green solution. Agent 16 crystallizes with water as the axial base; the water is eliminated when the Agent is dissolved in organic solvents. A labile orange-colored adduct is formed when a small quantity of pyridine is added to the green solution of Agent 16 or its chelate precursor. Agent 16 is stable in air, although loss of the ethyl group and oxidation of the residue occurs on prolonged storage at ambient temperatures.

Treatment of MMA with Agent 16 using the method of Example 4 yielded poly(MMA) with molecular weight with 9,700 and polydispersity of 2.3. A similar treatment of addition of pyridine (8 mg) yielded polymer with molecular weight of 8,600, compared to the molecular weight of 18,000 obtained by treatment in the absence of the Agent or pyridine.

Example 17

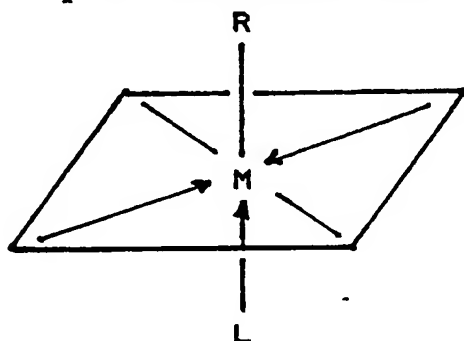
Bis[μ -[(2,3-butanedione dioximato)(2-)O:O']-tetrafluorodibonato(2-)-N,N',N'',N'''] (methanol)cobalt (II), Agent 17, was prepared by stirring an ice-cooled finely powdered mixture of cobaltous acetate tetrahydrate (2 g) and dimethylglyoxime (1.9 g) in a nitrogen-purged solution of boron trifluoride etherate (10 ml) in diethyl ether (150 ml) for 6 hours, followed by recrystallization of the filtered solids from methanol.

A deoxygenated mixture of MMA (100 g), AIBN (100 mg) and Agent 17 was added over a 3 hour period to hot butyl acetate maintained under nitrogen, followed by a 3 - 6 hour post-addition reaction period. The amounts of Agent, reaction temperatures, and average degrees of polymerization are shown in the Table:

	<u>Agent (mg)</u>	<u>Temperature (°C)</u>	<u>DP</u>
20	2.5	80	10
	5.0	80	5
	2.5	90	12
25	5.0	90	6

CLAIMS:

1. A process for the free radical polymerization of unsaturated monomers characterized in that there is used as an initiator and/or chain transfer agent in the process a transition metal complex comprising a metal cation and at least one chelating agent, said transition metal complex being generally in accordance with formula I



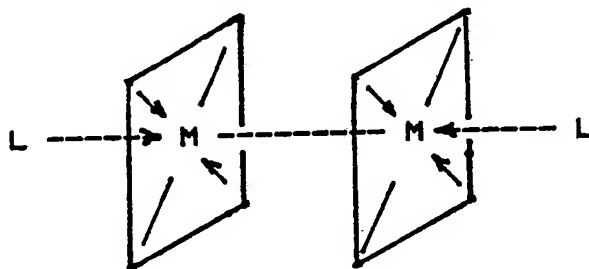
(I)

wherein M is a transition metal ion which can form hexa- or penta-coordinated structures and, when complexed in this manner, has two or more readily interconverted adjacent valence states, R is hydrogen or an organic group or a transition metal complex derived from formula I and L is a ligand for controlling the stability of an electron transfer properties of the transition metal complex and consists of an electron pair donor (Lewis base) capable of coordination with the metal ion.

2. A process as claimed in claim 1, characterized in that the complex of formula I comprises a metallic cation (M) coordinated with a

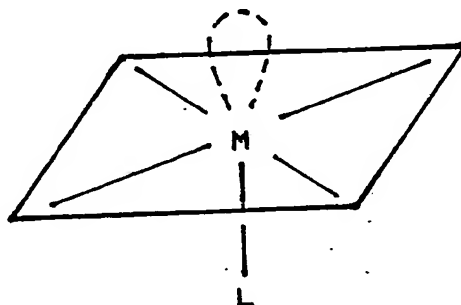
planar (equatorial), or approximately planar, arrangement of chelating ligands, R is a hydrogen atom or an organic moiety bound by a labile carbon-metal bond to the transition metal, and L is as stated in Claim 1.

3. A process as claimed in claim 1, characterized in that the transition metal complex has the dimeric structure of formula II



(II)

wherein the metallic cations M may be the same or different and each of the ligands L which may be the same or different are as defined in claim 1, and the complex is capable of dissociation to form (or may exist in equilibrium with) the monomeric species III



(III)

and/or is capable of reaction with radicals or other species present in the polymerizing system to form intermediates functionally equivalent to those of

formula I, as stated in claim 1.

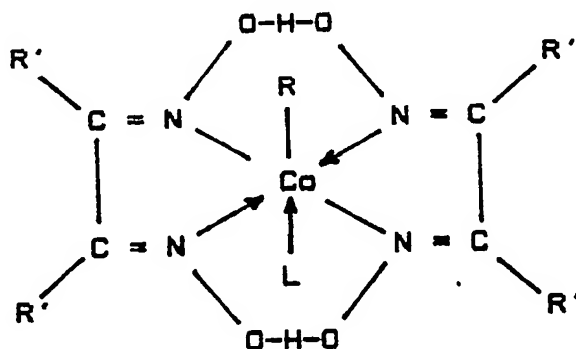
4. A process as claimed in any one of claims 1 to 3, characterized in that the transition metal is cobalt, rhenium or iridium.

5. A process as claimed in any one of claims 1 to 4, characterized in that the equatorial coordination is obtained from a single quadridentate chelating ligand, from two bidentate ligands, or from one bidentate ligand plus two monodentate ligands, or any other appropriate combination of ligands.

6. A process as claimed in claim 5, characterized in that the complex has no nett ionic charge and is soluble in non-polar or polar organic solvents.

7. A process as claimed in any one of claims 1 to 6, characterized in that the equatorial ligands are dioximes or other dicarbonyl or enolic carbonyl derivatives, or hydroxy, carboxy or enolic derivatives of azomethines (Schiff bases).

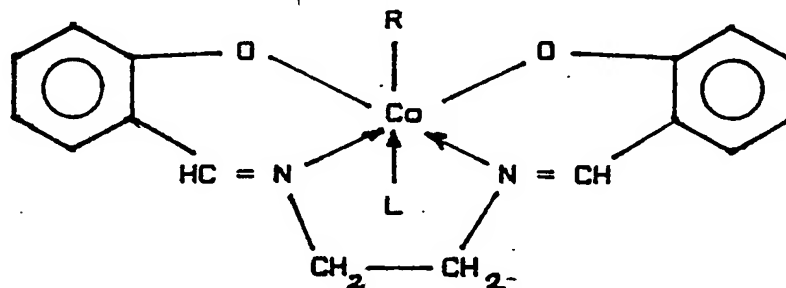
8. A process as claimed in claim 1, characterized in that the complex is a bis(dimethyl glyoxime) cobalt chelate of the formula IV



(IV)

wherein R and L are as defined in claim 1, and the groups R' are alkyl groups, and wherein the bridging hydrogen atoms may be optionally replaced by difluoroborate groups.

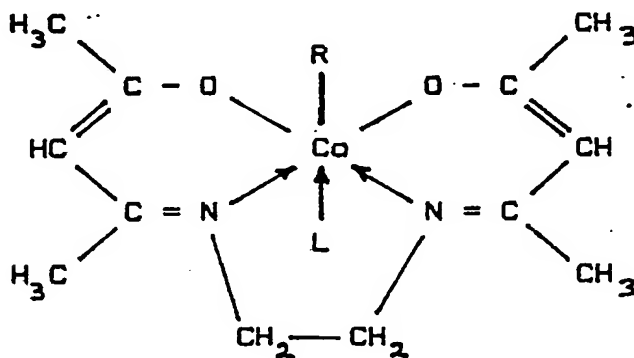
9. A process as claimed in claim 1, characterized in that the complex is a salicylaldehyde-diamine chelate of the formula V



(V)

wherein R and L are as defined in claim 1.

10. A process as claimed in claim 1, characterized in that the complex is an acetylacetone-diamine chelate of formula VI



(VI)

wherein R and L are as defined in claim 1.

11. A process as claimed in any one of the preceding claims, characterized in that the group R is an alkyl, aryl, or heterocyclic species, or a substituted derivative of one of these species which is capable of homolytic dissociation from the metal ion on heating or on irradiation with visible or ultraviolet light, or a halide or other anion bound to the chelates metal ion.

12. A process as claimed in claim 11, characterized in that R is an alkyl group bearing one or more nitrile, ester, aromatic or substituted aromatic groups substituents on the carbon atom bound to the metal ion.

13. A process as claimed in any one of the preceding claims, characterized in that the axial ligand L consists of water, an alcohol or other hydroxylic species, a thioether, amine, phosphine, carbonyl or carboxylate, or any other electron pair donor (Lewis base) capable of coordination with the metal ion which does not inhibit dissociation of the opposing axial ligand.

14. A process as claimed in claim 13, characterized in that the ligand L is a weakly basic tertiary amine.

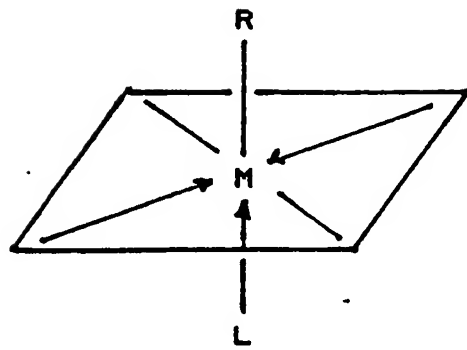
15. A process as claimed in any one of claims 1 to 12, characterized in that the ligand L is derived in situ from a monomer or another species present in the polymerization mixture.

16. Oligomers derived from unsaturated monomers characterized in that they contain terminal unsaturation and have a degree of polymerization of from 2 to 200.

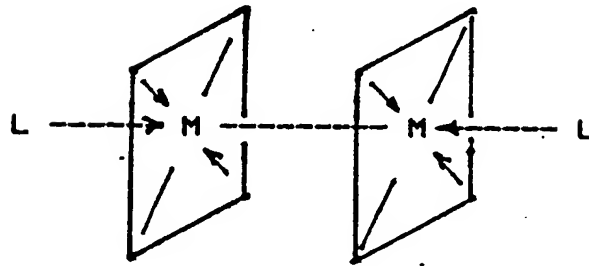
17. Oligomers as claimed in claim 16, characterized in that they are derived from methacrylic acid, methacrylate esters, methacrylamide, methacrylonitrile, acrylic esters, acrylamide, acrylonitrile, vinyl esters, vinylaromatics, vinyl halides or mixtures of any two or more of said monomers.

18. Oligomers whenever produced by the process claimed in any one of claims 1 to 15.

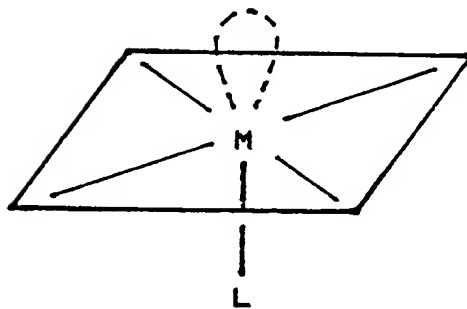
1/2



(I)

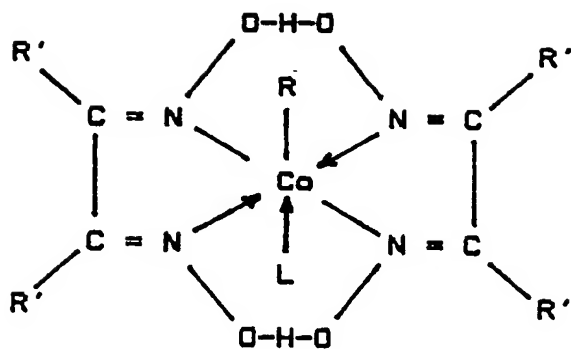


(II)

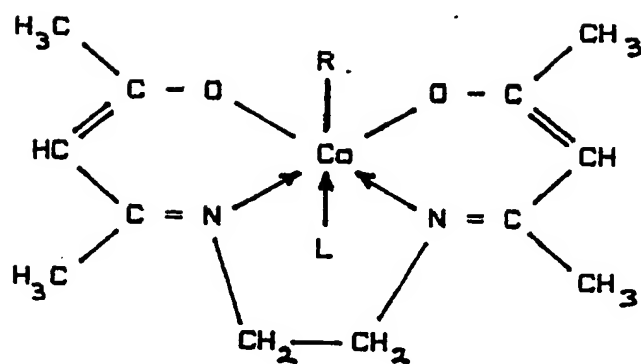


(III)

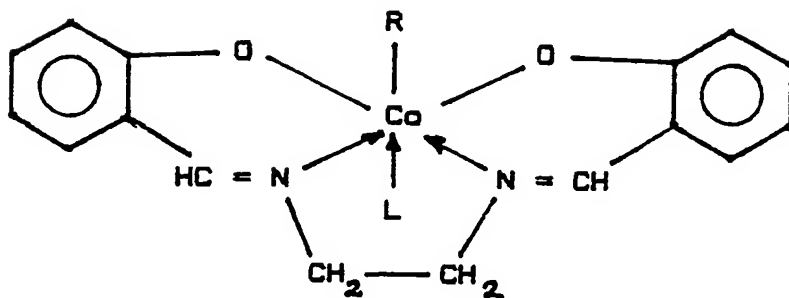
2/2



(IV)



(VI)



(V)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/AU86/00372

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC <div style="text-align: center; font-family: monospace; font-size: 1.2em;">Int. Cl.⁴ C08F 4/80 // C08F 2/38</div>						
II. FIELDS SEARCHED <div style="text-align: center; font-size: 0.8em;">Minimum Documentation Searched †</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; text-align: left; padding: 5px;">Classification System</th> <th style="text-align: left; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="padding: 10px; vertical-align: top;">IPC</td> <td style="padding: 10px; vertical-align: top;">C08F 4/72, 4/74, 4/76, 4/78, 4/80, 4/82</td> </tr> </table> <div style="text-align: center; font-size: 0.8em; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</div>			Classification System	Classification Symbols	IPC	C08F 4/72, 4/74, 4/76, 4/78, 4/80, 4/82
Classification System	Classification Symbols					
IPC	C08F 4/72, 4/74, 4/76, 4/78, 4/80, 4/82					
AU: IPC as above; Australian Classification 09.4 - 22						
III. DOCUMENTS CONSIDERED TO BE RELEVANT †						
Category *	Citation of Document, †† with Indication, where appropriate, of the relevant passages †‡	Relevant to Claim No. ‡‡				
X	US, A, 4526945 (CARLSON) 2 July 1985 (02.07.85)	(1-2, 4-8, 11-15, 18)				
P,X	EP, A, 196783 (E.I. DU PONT DE NEMOURS AND COMPANY) 8 October 1986 (08.10.86) whole document	(1-15, 18)				
P,X	EP, A, 199436 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 October 1986 (29.10.86) whole document	(1-15, 18)				
A	GB, B, 1199387 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 22 July 1970 (22.07.70) See pages 3-4	(1-15, 18)				
A	US, A, 4169092 (BAYER) 25 September 1979 (25.09.79)	(1-15, 18)				
A	AU, B, 47610/64 (294613) (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 3 February 1966 (03.02.66)	(1-15, 18)				
<div style="display: flex; justify-content: space-between; font-size: 0.8em;"> <div style="width: 45%;"> <p>* Special categories of cited documents: †‡</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search <div style="text-align: center; font-family: monospace;">2 March 1987 (02.03.87)</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-family: monospace; font-size: 1.2em;">10.3.87 (10 MARCH 1987)</div>				
International Searching Authority <div style="text-align: center; font-weight: bold;">AUSTRALIAN PATENT OFFICE</div>		Signature of Authorized Officer <div style="text-align: center;">J. BODEGRAVEN </div>				

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

Claims 16 and 17 include products not produced by the process of claims 1-15.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers: 1-15, 18

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest.

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 86/00372

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document
Cited in Search
Report

Patent Family Members

AU 47610/64	BE 651281
-------------	-----------

US 4169092	US 4169092
------------	------------

GB 1199387	BE 719541	DE 1793217	FR 1576988
	GB 1199387	NL 6811660	US 3472876

EP 196783	EP 199436	JP 61228006	JP 61241302
-----------	-----------	-------------	-------------

END OF ANNEX